PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : B41M 5/00, 3/00, C09D 11/00

A1

(11) International Publication Number: WO 99/64249

(43) International Publication Date: 16 December 1999 (16.12.99)

(21) International Application Number: PCT/US99/13214

(22) International Filing Date: 10 June 1999 (10.06.99)

(30) Priority Data:
09/096,128 11 June 1998 (11.06.98) US

(71) Applicant: LEXMARK INTERNATIONAL, INC. [US/US]; 740 West New Circle Road, Lexington, KY 40550 (US).

(72) Inventors: BEACH, Bradley, Leonard; 1757 Hawthorne Lane, Lexington, KY 40505 (US). HOLLOWAY, Ann, P.; 1136 Chetford Drive, Lexington, KY. 40509 (US). MACMILLAN, David, Starling; 240 Buffalo Trace, Winchester, KY 40391 (US). SUTHAR, Ajay, Kanubhai; 3805 Hapgood Lane, Lexington, KY 40514 (US). WEISMAN, Mark, Stephen, Jr.; 1521 Continental Square #50, Lexington, KY 40505 (US).

(74) Agent: SANDERSON, Michael, T.; Lexmark International, Inc., 740 West New Circle Road, Lexington, KY 40550 (US).

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: COATING SYSTEM FOR INK JET APPLICATIONS

(57) Abstract

A method for coating substrates with a solution comprising a reactant is described. The reactant is an acid, a base, a polyvalent metal salt or polyelectrolyte and the coated substrates result in superior print images when used in ink jet printers.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania
AM	Armenia
AT	Austria
AU	Australia
AZ	Azerbaijan
BA	Bosnia and Herzegovina
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
BY	Belarus
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CN	China
CU	Cuba
CZ	Czech Republic
DE	Germany
DK	Denmark
EE	Estonia
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GE	Georgia
GH	Ghana
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IL	Israel
IS	Iceland
IT	Italy
JP	Japan
KE	Kenya
KG	Kyrgyzstan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
KZ	Kazakstan
LC	Saint Lucia
LI	Liechtenstein
LK	Sri Lanka
LR	Liberia
LS	Lesotho
LT	Lithuania
LU	Luxembourg
LV	Latvia
MC	Monaco
MD	Republic of Moldova
MG	Madagascar
MK	The former Yugoslav Republic of Macedonia
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
MX	Mexico
NE	Niger
NL	Netherlands
NO	Norway
NZ	New Zealand
PL	Poland
PT	Portugal
RO	Romania
RU	Russian Federation
SD	Sudan
SE	Sweden
SG	Singapore
SI	Slovenia
SK	Slovakia
SN	Senegal
SZ	Swaziland
TD	Chad
TG	Togo
TJ	Tajikistan
TM	Turkmenistan
TR	Turkey
TT	Trinidad and Tobago
UA	Ukraine
UG	Uganda
US	United States of America
UZ	Uzbekistan
VN	Viet Nam
YU	Yugoslavia
ZW	Zimbabwe

COATING SYSTEM FOR INK JET APPLICATIONS

FIELD OF THE INVENTION

This invention relates to a novel method for printing and the related print image produced therefrom. Specifically, the invention is directed to a method for reducing substrate sensitivity and for producing print images with improved optical densities, drying times, waterfastness and/or chroma.

BACKGROUND OF THE INVENTION

Conventional ink jet imaging processes may be deficient in that they are unable to print uniformly well on a wide variety of commercially available substrates, such as paper. Image density, dry time, chroma and other characteristics can change substantially because these characteristics depend on substrate properties which vary greatly depending on the type of substrate being used.

Quicker ink penetration into the substrate typically results in a faster ink drying time, but often causes the ink's colorant (e.g., pigment or dye) to disperse or penetrate more quickly into the bulk of the substrate, like paper, leaving less colorant on the substrate surface and thereby resulting in an image having, for example, a low optical density. Moreover, faster ink drying time can result in the undesired spreading of ink along paper fibers and thereby result in the feathering or bleeding (mixing) of inks of different colors. If the ink penetrates slowly, however, the drying time becomes longer and this often results in poor print quality resulting from, for example, smudges, print offset, and smear.

It is of increasing interest to develop a method for printing that allows for inks to dry well, not bleed and result in denser print images on a variety of substrates.

This invention, therefore, is directed to a novel method for printing which unexpectedly results in superior print images that dry well and display excellent optical densities and higher chroma on many types of substrates.

BACKGROUND REFERENCES

Several methods of modifying a substrate or ink during imaging are known. U.S. Patent No. 4,382,262 discloses a method for ink jet printing with a plurality of colors. The substrate is given a surface composition comprising a chemical agent capable of converting a first colorless ink to a first color and a second colorless ink to a second color.

U.S. Patent No. 4,694,302 discloses a method of increasing the waterfastness and print quality of a dye containing ink. A reactive species reacts with a component in the substrate or vice versa to form a polymer that binds the dye in the ink to the resultant polymeric lattice.

U.S. Patent Nos. 5,320,668 and 5,181,045 disclose a method for preventing bleeding of ink colorants. The method forces colorant in a first ink out of solution by contacting a border of a printed first ink with a second ink having an appropriate pH.

U.S. Patent No. 5,006,862 discloses a method for improving waterfastness and smear-resistance of an ink by treating a substrate with a basic solution having about 90% to about 100% by weight of a mono-hydroxy alcohol.

U.S. Patent No. 4,538,160 discloses an ink jet recording apparatus comprising an ink jet nozzle for jetting colored ink and a liquid jetting nozzle for jetting a processing liquid.

OBJECT OF THE INVENTION

A first object of the present invention is to provide a method for producing denser print images by reducing substrate sensitivity, i.e., denser images that print uniformly well on a wide variety of commercially available substrates, even with improved drying times. In this invention, denser print images are defined to mean print images having improved optical densities (black inks) and improved chroma (color inks).

A second object of the present invention is to reduce intercolor bleed of inks printed on a substrate.

A third object of the present invention is to increase the waterfastness of dye-based inks.

A fourth object of the present invention is to improve ink drying times.

SUMMARY OF THE INVENTION

In a first aspect, this invention is directed to a method which comprises the steps of applying, in no particular order, to a substrate,

(a) a solution comprising a reactant; and

(b) an ink comprising a colorant,

with the proviso that when said colorant is a dye, said reactant is not a polyvalent metal salt.

Often, when an acidic ink is applied, said solution comprising a reactant is, preferably, alkaline and when an alkaline ink is applied, said solution comprising a reactant is, preferably, acidic.

In a second aspect, this invention is directed to a substrate having a solution comprising a reactant coated thereon.

In a third aspect, this invention is directed to a print image produced from the first aspect of this invention.

It is noted herein that the solution comprising a reactant is not required to be, and preferably is not, a solution which is: an ink, polymer forming, protective layer forming or capable of breaking hydrogen bonds in a substrate like paper. The solution comprising a reactant is not required to comprise, and preferably, does not comprise about 90.0% or more by weight of a mono-hydroxy alcohol. Also, the solution comprising a reactant can have, but is not required to have, both a cationic polymer and a polyvalent metal salt when a dye-based ink is used.

DETAILED DESCRIPTION OF THE INVENTION

There is no limitation with respect to the order the solution comprising a reactant and the ink are applied to the substrate. Often, however, the solution comprising a reactant is applied before the ink.

The pH differential between the ink and solution comprising a reactant is often less than about 8.0, and preferably ranges from about 1.0 to about 6.5. When an acidic solution is employed, the acidic solution often comprises a mild acid as the reactant, whereby a mild acid is defined to mean an acid having a pH of greater than about 3.0 and less than about 7.0, and preferably, greater than about 4.0 and less than about 5.0.

When a basic solution is employed, the basic solution often comprises a mild base as the reactant, whereby a mild base is defined to mean a base having a pH of greater than about 7.0 and less than about 11.0, and preferably, greater than about 8.0 and less than about 10.0.

The pH of the mild acids and mild bases described in this invention mean the pH values obtained by testing the pH (with a commercially available glass electrode pH meter) of a homogeneous solution (50:50 weight percent ratio) of mild acid or mild base and deionized water.

When the solution comprising a reactant is an acidic solution made with, for example, a mild acid, the mild acid which may be employed is generally only limited to the extent that it will result in a solution comprising a reactant capable of flocculating a dispersed pigment or precipitating a dye. An illustrative list of the types of acids which may be employed in this invention includes acetic, acetoacetic, acrylic, adipic, alloxanic, aminobenzoic, anisic, ascorbic, aspartic, barbituric, benzoic, butyric, caproic, chloracetic, chlorobenzoic, chlorobutyric, chlorocinnamic, chlorophenoxyacetic, chlorophenylacetic, chloropropionic, cinnamic, citric, crotonic, cyclohexane-dicarboxylic, cyclopropane-dicarboxylic, dihydroxybenzoic, dimethylmalic, dimethylmalonic, ethylbenzoic, ethylphenylacetic, formic, fumaric, furancarboxylic, furoic, gallic, glutaramic, glutaric, glycolic, heptanoic, hexanoic, hydroxybenzoic, hydroxybutyric, hydroxypropionic, iodoacetic iodobenzoic, itaconic, lactic, lutidinic, maleic, malic, malonic, mandelic, mesaconic, methylcinnamic, methylglutaric, methylmalonic, methylsuccinic, napththoic, nonanic, octanoic, oxalic, phenylacetic, phenylbenzoic, phenylbutyric, phenylpropionic, phthalic, picric, pimelic, propionic, quinolinic, suberic, succinic, tartaric, terephthalic, thioacetic, thiophenecarboxylic, toluic, trimethylacetic, uric, valeric and vinylacetic acid.

Mixtures of the above-acids may also be employed, and acetic acid and glycolic acid are typically the most preferred.

When the solution comprising a reactant is a basic solution made with, for example, a mild base, the mild base, which may be employed, is generally only limited to the extent that it will result in a solution comprising a reactant capable of flocculating a dispersed pigment or precipitating a dye. An illustrative list of mild bases which may be employed in this invention includes amylamine, azetidine, 2-aminoethyl benzene, benzylamine, bornylamine, brucine, 1-amino-3-methyl butane, 2-amino-2-methyl butane, 1,4-diamino butane, butylamine, chlortriethylammonium, codeine, n-butyl cyclohexaneamine, cyclohexylamine, decylamine, diethylamine, diisobutylamine, diisopropylamine, dimethylamine, dodecaneamine, ephedrine, 1-amino-3-methoxy ethane, 1,2-bismethylamino ethane, 2-amino ethylamine, ethylamine, ethylenediamine, glutamine, dimethyl glycine, 1-amino heptane, 2-amino heptane, 2-methylamino heptane, hexadecaneamine, hexamethylenediamine, hexylamine, imidazol, 1-amino indane, methylamine, morpholine, neobornylamine, nonylamine, octadecaneamine, octylamine, 3-amino pentane, 3-amino-3-methyl pentane, pentadecylamine, piperazine, piperidine, 1-n-butyl piperidine, 1,2-dimethyl piperidine, 1-ethyl piperidine, 1-methyl piperidine, 1,3-diamino propane, 1,2,3-triamino propane, propylamine, 4-amino pyridine, 4-methylamino pyridine, pyrrolidine, 1,2-dimethyl pyrrolidine, n-methyl pyrrolidine, quinine, tetradecaneamine, tridecaneamine, polyethylenimine, polymer prepared from dimethyldiallylammonium chloride, or mixtures thereof. Polyethylenimine (Lupasol™FG, or PR 8515 commercially available from BASF) and polymer prepared from dimethyldiallylammonium chloride (commercially available from Cytec Industries) are typically the most preferred.

In a preferred embodiment, when an acidic or basic solution is employed, the solutions preferably comprise as the reactant, at least one polyvalent metal salt which typically renders the solution acidic or basic. Such polyvalent metal salts are only limited to the extent that they will result in a solution comprising a reactant that is capable of flocculating a dispersed pigment or precipitating a dye. When an acidic solution is desired, the polyvalent metal salts typically include group IIA, IIIA or transition metal salts, such as calcium chloride, magnesium chloride, and preferably, aluminum chloride. When a basic solution is desired, the polyvalent metal salts typically include group IIA, group IIIA or transition metal salts like hydroxides, nitrates and sulfates of the same,

including calcium hydroxide, calcium nitrates, magnesium hydroxide, magnesium nitrates, sodium hydroxide and sodium nitrates. Mixtures of the above polyvalent metal salts may also be used.

In another preferred embodiment, when an acidic or basic solution is employed, the solutions preferably comprise as the reactant, at least one polyelectrolyte which typically renders the solution acidic or basic. When an acidic solution is desired, the polyelectrolyte is typically cationic. When a basic solution is desired the polyelectrolyte is typically anionic. There is generally no limitation with respect to the polyelectrolytes employed in this invention other than that the polyelectrolytes result in a solution comprising a reactant which is capable of flocculating a dispersed pigment or precipitating a dye.

The polyelectrolytes which may be used in this invention are those which often have nitrogen as the charge source. They typically have a weight average molecular weight of greater than about 300 and less than about 10,000,000. Preferably, the polyelectrolytes have a weight average molecular weight of greater than about 1,000 and less than about 200,000, and most preferably, greater than about 5,000 and less than about 15,000, including all ranges subsumed therein. Also, the polyelectrolytes may be homopolymers, copolymers (including terpolymers), random or block polymers, immiscible or miscible blends as well as straight chain or branched polymers. Their respective backbones are generally not limited and include those which are atactic, isotactic or syndiotactic in nature.

An illustrative list of cationic polyelectrolytes which may be employed in this invention include those with tertiary amino or quaternary ammonium groups prepared from, for example, precursor monomers selected from the group consisting of quaternary diallyldialkylammonium halides like diallyldimethylammonium chloride, N-alkylammonium chlorides, methacrylamidopropyltrimethylammonium chloride, methacryloxyethyl trimethylammonium chloride, 2-hydroxy-3-methacryloxypropyl trimethylammonium chloride, methacryloxyethyl trimethylammonium methosulfate, vinylbenzyltrimethylammonium chloride and quaternized 4-vinylpyridine. Such cationic polyelectrolytes are further described in United States Patent No. 4,554,181, the disclosure of which is incorporated herein by reference.

The preferred cationic polyelectrolytes which may be employed in this invention include those which may be classified as polyimines, polyamines or quaternary

polyamines, with tetraalkylated quaternary polymers (i.e., quats or polyquats) being especially preferred.

The polyimines which may be employed in this invention include acids or ammonium salts of polyalkylenimines. Preferred polyalkylenimines are acidified or ammonium salts of polyethylenimines sold under the name Lupasol™ and commercially available from BASF.

The polyamines which may be employed in this invention include those which can be prepared from, for example, precursors like alkylene dihalides and ammonia. The resulting polymers will be polyamines or polyquats, depending on the extent of branching. Other polyamines which may be employed in this invention include those which can be prepared from precursor monomers such as alkylenediamines and at least one monomer selected from the group consisting of alkylene dihalides and epichlorohydrin. Still other polyamines which may be used in this invention include those which can be prepared from precursor acrylamides, aldehydes and dialkylamines (for example, by way of a Mannich reaction), as well as those which can be prepared from acrylamide and aminoalkylacrylates, or aldehydes and melamine.

A preferred list of such polyamines (cationic polyelectrolytes) includes those which are the reaction product of ethylenedichloride and ammonia (EDC/NH_3), ethylenedichloride and alkylenedichloride (EDC/AC), alkylenediamine and epichlorohydrin (AD/EPI), acrylamide and aminoethylacrylate (AM/AEA), acrylamide and dimethylaminoethylmethacrylate (AM/DMAEMA) and melamine and formaldehyde (MF). Another polyamine which may be used is aminomethylated polyacrylamide (AMPAM).

The quaternary polyamines which may be employed in this invention include those which can be prepared by, for example, polymerizing dialkylamines and epichlorohydrin, or by polymerizing dialkyldiallylammonium halides, either alone or in the presence of acrylamides to produce a copolymer. Still other quaternary polyamines which may be employed in this invention include those which may be prepared from acrylamides and acryloxyalkyltrialkylammoniumalkyl sulfates or acryloxyalkyltrialkylammonium halides.

The preferred quaternary polyamines (cationic polyelectrolytes) include those which are the reaction product of dimethylamine and epichlorohydrin (DMA/EPI), acrylamide and dimethyldiallylammonium chloride (AM/DMDAAC), acrylamide and 2-

acryloxyethyltriammoniummethyl sulfate (AM/AETAMS), acrylamide and 2-methylacryloxyethyltrimethylammoniummethyl sulfate (AM/METAMS), acrylamide and 2-methylacryloxyethyltrimethylammonium chloride (AM/METAC), and acrylamide and 3-methylacryloxy-2-hydroxypropyltrimethylammonium chloride (AM/MAPTAC). Another quaternary polyamine which may be used is a polymer prepared from dimethyldiallylammonium chloride (DMDAAC). The most preferred quaternary polyamine is DMA/EPI, sold under the name Superfloc flocculant (e.g. C-567, C-573 and C-581) and commercially available from Cytec Industries.

The anionic polyelectrolytes which may be employed in this invention include those which can be prepared by, for example, hydrolyzing an acrylamide or by copolymerizing acrylamides and acrylic acid.

The polyelectrolytes which may be employed in this invention may be prepared via art recognized reactions which include free radical polymerizations, Michael reactions, Mannich reactions or by hydrolyzing precursor polymers. A more detailed description of the synthesis of such polyelectrolytes is found in <u>American Petroleum Institute Publication</u>, No. 420, 1st edition, August 1990, the disclosure of which is incorporated herein by reference. Additionally, such polyelectrolytes are commonly available from, for example, Cytec Industries.

It is noted herein that any combination of reactants may be employed in the solution comprising a reactant as long as the solution results in the flocculation of a dispersed pigment or precipitation of a dye. However, when an ink comprising a dye as the colorant is used, it is preferred that the solution comprising a reactant does not comprise a polyvalent metal salt as the reactant.

When preparing the above-described solutions comprising a reactant, the solutions, in the absence of polyelectrolytes, often have from about 0.1% to about 35.0%, and preferably, from about 0.2% to about 25.0%, and most preferably, from about 1.0% to about 20.0% by weight of reactant, based on total weight of the solution comprising a reactant, including all ranges subsumed therein.

When preparing the above-described solutions comprising a reactant, the solutions, when using only polyelectrolytes as the reactant, typically comprise from about 0.5% to about 85.0% by weight reactant, and preferably, from about 10.0% to about 50.0% by weight reactant, and most preferably, from about 20.0% to about 30.0% by

weight reactant, based on total weight of the solution comprising a reactant, including all ranges subsumed therein.

When the above-described solutions comprising a reactant have mixtures of reactants, the amount of each reactant employed is generally only limited to the extent that the resulting solution comprising a reactant is capable of flocculating a dispersed pigment or precipitating a dye.

When mild acids or bases are the reactants, the solutions comprising a reactant typically comprise, in addition to the reactant, water and less than about 30.0% by weight of a C_{1-6} organic alcohol based on total weight of the solution comprising a reactant. Preferably, when the solution comprises a mild acid or base as the reactant, no more than about 15.0 % by weight, and most preferably, no more than about 5.0 % by weight is a C_{1-6} organic alcohol, such as n-propanol.

When a polyvalent metal salt, a polyelectrolyte or both (i.e., a pigment is used as the colorant) is employed as the reactant(s), the solution comprising a reactant typically comprises, in addition to the reactant, a balance that substantially comprises an organic solvent. The only limitation with respect to the organic solvents employed is that they result in a solution capable of flocculating a dispersed pigment or precipitating a dye. An illustrative list of organic solvents which can be employed include polyalcohols like 1,2-propanediol, 1,2,3-propanetriol and sorbitol, and preferably, alkylene glycols like diethylene glycol.

In the case of pigment-based inks, and when a polyvalent metal salt and a polyelectrolyte are used as reactants in the solution comprising a reactant, the amount of each reactant used with respect to each other is only limited to the extent that the resulting solution is capable of flocculating a dispersed pigment. Often, the weight percent ratio of polyvalent metal salt to polyelectrolyte is from about 1:99 to about 99:1, with a 15:85 to about 85:15 weight percent ratio being most preferred. Also, when both a polyvalent metal salt and a polyelectrolyte are used as reactants in a solution comprising a reactant, the total weight percent of polyvalent metal salt and polyelectrolyte (based on total weight of the solution comprising a reactant) is greater than about 0.5% and less than about 30.0%, including all ranges subsumed therein.

Moreover, it is within the scope of this invention to add to the solution comprising a reactant art recognized ink additives. Such ink additives include biocides, fungicides, bacteriocides, penetrants, including 1,2-hexanediol, anti-kogation agents,

anti-curling agents, buffers, chelating agents, anti-bleed agents, pH modifiers and the like.

A most preferred additive which may be added to the solution comprising a reactant is, however, a surfactant. There generally is no limitation with respect to the type or amount of surfactant added as long as the resulting solution comprising a reactant is capable of flocculating a dispersed pigment or precipitating a dye. The surfactants employed are often selected from the group consisting of anionic, cationic, nonionic and amphoteric surfactants. The anionic surfactants include carboxylic acids and soaps; sulfated esters, amides, alcohols, ethers and carboxylic acids; sulfonated petroleum, aromatic hydrocarbons, aliphatic hydrocarbons, esters, amides, amines, ethers, carboxylic acids, phenols and lignins; acylated polypeptides; and phosphates. The cationic surfactants include amines, amine salts, trialkylamine oxides, n-polyethoxylated long chain amines, quaternary ammonium salts, heterocyclic amines, alkylolamine-fatty acid condensates, alkyl phosphonamides, amphoterics, perfluoro compounds, sequestrants, silicones and inorganic cationics. The nonionic surfactants include esters of polyhydric alcohols; alkoxylated amides; esters of polyoxyalkylene, polyoxypropylene and polyoxyalkylene glycols; tertiary acetylenic glycols; and polyoxyethylated alkyl phosphates.

The surfactants most often employed are selected from the group consisting of polyhydrics (including alkyne polyols), polyethers, alkylamine alkoxylates, polysiloxanes and halogenated alkyl alkoxylates. The preferred surfactants include polyalkylsiloxanes, polyethers, alkyne polyols and halogenated alkyl alkoxylates.

The polyalkylsiloxane-based surfactants which may be employed in this invention are often modified polyorganosiloxanes having polyalkylene oxides grafted thereon via hydrosilation reactions. Such a surfactant is typically a polyether modified polydimethylsiloxane sold under the name SILWET® (e.g., L-77, L-720, L-722, L-7001, L-7087, L-7600, L-7606) and commercially available from OSi Specialties. These types of surfactants vary in molecular weight, but often have a weight average molecular weight from about 600 to about 20,000.

The polyether-based surfactants which may be employed in this invention include those prepared from secondary alcohols and alkylene oxides such as linear secondary alcohols and ethylene oxides. The polyether-based surfactants vary in molecular weight and are identified by Chemical Abstract No. 84133-50-6. Such polyether-based

surfactants are sold under the name TERGITOL® (e.g., 15-S-3, 15-S-7, 15-S-9, 15-S-12) and are commercially available from Union Carbide.

The alkyne polyol-based surfactants which may be employed in this invention have hydrophobic and hydrophilic segments, and they vary in molecular weight. They are sold under the name SURFȲNOL® (e.g., 440, 465) and are commercially available from Air Products and Chemicals, Inc.

The halogenated alkyl alkoxylate-based surfactants which may be used in this invention are often perfluorinated or fluorinated. They are sold under the name FLOURAD™ (e.g., FC-171, FC-430), vary in molecular weight, and are commercially available from 3M.

The amount of surfactant employed in the solution comprising a reactant is often from about 0.05 % to about 4.5 % by weight, and preferably, from about 0.5 % to about 3.5 % by weight, and most preferably, from about 1.0 % to about 3.0 % by weight, based on total weight of the solution comprising a reactant, including all ranges subsumed therein. It is noted that when calculating the weight percent of surfactant employed, the calculation is based on the form (i.e., composition) of surfactants made commercially available.

There generally is no limitation with respect to how the solution comprising a reactant is made as long as the resulting solution is capable of flocculating a dispersed pigment or precipitating a dye. Essentially, the components (e.g., reactant, water, surfactant and polyalcohol, as the case may be) are added, in no particular order, to a mixing vessel like a beaker. The components may be, for example, mixed, stirred or agitated at ambient temperature and atmospheric pressure; however, temperature and pressure variations may be made in order to enhance the formation of the solution comprising a reactant.

There is essentially no limitation with respect to the pigment or dye containing inks which may be used to print with the solutions comprising a reactant of this invention. The only limitation regarding the inks is that they may be used for printing on a substrate.

The inks which may be used with the solutions comprising a reactant of this invention, whether dye-based or pigment-based, may comprise art recognized additives. Such art recognized additives include, for example, dispersants, humectants like glycerol

and sorbitol, biocides, fungicides, bacteriocides, penetrants like 1,2-hexanediol and acetylene derived compounds, surfactants like polyorganosiloxanes, anti-kogation agents, anti-curling agents, buffers, chelating agents and anti-bleed agents.

The inks used with the solutions of this invention may be aqueous or non-aqueous. Therefore, the balance of the ink compositions will comprise water when aqueous inks are desired. When non-aqueous inks are desired, their balance will comprise, for example, organic solvents such as polyethylene glycol, glycerol or 2-pyrrolidinone. Also, when non-aqueous inks are desired, oils such as mineral oil, tung oil and soybean oil may be employed.

There is no limitation with respect to the pigments that may be employed in the inks used in conjunction with this invention other than that they are capable of resulting in an ink which may be printed on a substrate. Any of the commonly employed organic or inorganic pigments may be used. An illustrative list of the pigments which may be employed includes azo pigments such as condensed and chelate azo pigments; polycyclic pigments such as phthalocyanines, anthraquinones, quinacridones, thioindigoids, isoindolinones and quinophthalones. Still other pigments which may be employed include, for example, nitro pigments, daylight fluorescent pigments, carbonates, chromates, titanium oxides, zinc oxides, iron oxides and carbon black. Such pigments may be prepared via conventional techniques and are commercially available.

The amount of pigment employed in such inks is limited only to the extent that the amount results in an ink capable of being printed on a substrate. Often the amount of pigment employed is from about 0.2 % to about 10.0 % by weight, and preferably, from about 0.5 % to about 6.0 % by weight, and most preferably, from about 1.0 % to about 5.0 % by weight based on total weight of the ink composition, including all ranges subsumed therein.

There is no limitation with respect to the dye compounds which may be employed in the inks used in conjunction with this invention other than that they are capable of resulting in a print image. An illustrative list of such dyes includes, for example, nitro dyes; nitroso dyes; azo dyes such as monoazo or polyazo dyes, mordant dyes, preformed metal complexes, pyrazolones and stilbenes; thiazoles; diphenylmethanes; triphenylmethanes; xanthenes; acridines; azines; oxazines; thiazines; quinones and indigoids. Such dyes are art recognized and commercially available. Many of these dyes

are described in, for example, The Chemistry of Synthetic Dyes, by K. Venkataraman, Academic Press Inc., 1953.

The amount of dye compound employed is limited only to the extent that the resulting inks may be used to print on a substrate. Often, the amount of dye compound employed is from about 0.2 % to about 20.0 % by weight, and preferably, from about 0.5 % to about 15.0 % by weight, and most preferably, from about 1.0 % to about 10.0 % by weight based on total weight of the ink composition, including all ranges subsumed therein.

When making pigment-based inks, it is desirable to employ dispersants in the inks to prevent the pigment from settling in the ink composition. There is essentially no limitation with respect to the amount of dispersant employed other than that the amount of dispersant used results in an ink composition capable of being printed on a substrate. When making a pigment-based ink, typically from about 0.05 % to about 7.0 %, and preferably, from about 0.1 % to about 6.0 %, and most preferably, from about 0.2 % to 4.0 % by weight of dispersant is employed based on total weight of the ink composition, including all ranges subsumed therein.

There is essentially no limitation with respect to the dispersants which may be employed in this invention. In fact, any non-polymeric or polymeric dispersant which may be used to make a pigment-based ink composition may be employed in this invention. The often preferred dispersants are polymeric dispersants. An illustrative list of such polymeric dispersants includes random, block and branched polymers, whereby the polymers may be anionic, cationic or nonionic in nature. The polymeric dispersants typically have hydrophilic segments for aqueous solubility and hydrophobic segments for pigment interaction. Moreover, polymeric dispersants as used herein are meant to include homopolymers, copolymers (including terpolymers), immiscible blends and miscible blends.

Since the polymeric dispersants are generally limited only to the extent that they are capable of dispersing a pigment in an ink composition, the precursor units which may be used to make such polymeric dispersants are not limited. Precursor, as used herein, is meant to include monomeric and macromeric units.

A general list of the monomeric units which may be employed to make such polymeric dispersants include, for example, acrylic monomers, styrene monomers and

monomers having amine groups. Illustrative examples of the monomers which may be employed include acrylic and methacrylic acid, acrylamide and methacrylamide.

The polymeric dispersants often employed tend to be any of those which are commercially available as well as the polymeric dispersants which may be made via conventional techniques which include, for instance, anionic, group transfer or free radical polymerizations of monomeric units.

The often preferred polymeric dispersants which may be employed in this invention are random polymers prepared from three precursors. The most preferred precursors include monomeric and macromeric precursors, including at least one member selected from the group consisting of acrylates and methacrylates, at least one member selected from the group consisting of acryloyl- and methacryloyl-terminated polydimethylsiloxanes and at least one member selected from the group consisting of stearyl acrylate, stearyl methacrylate, lauryl acrylate and lauryl methacrylate. Dispersants prepared with methacrylate, methacryloyl-terminated polydialkylsiloxane and stearyl methacrylate (22:1:1 molar ratio, respectively) are most preferred.

The polymeric dispersants prepared from these precursors may be made by polymerizing the monomeric and macromeric precursors via art recognized techniques which include free radical polymerizations. A more detailed description of the most preferred polymeric dispersants which may be employed in this invention may be found in U.S. Patents Nos. 5,714,538 and 5,719,204, assigned to Lexmark International, Inc., the disclosures of which are incorporated herein by reference.

There is no limitation with respect to how the ink compositions are made. Essentially, the components (e.g., pigment, biocide, water) of the inks are, for example, mixed, stirred or agitated using any art recognized technique. The inks may be made at ambient temperature, atmospheric pressure or at any pressure or temperature variations which may result in ink formation. The addition of the components is not limited to any particular order, with the proviso that the resulting composition is one which may be employed to print on a substrate.

Moreover, none of the conventional processing steps is meant to be ignored when preparing the ink compositions used in this invention. Therefore, for example, it is within the scope of this invention to grind pigments to their desired particle/agglomerate sizes via art recognized milling processes. It is also within the scope of this invention to

mix the pigments with the polymeric dispersants of choice prior to combining the pigments with any other components of the inks.

In a preferred embodiment of this invention, a basic ink is employed with a pigment as the colorant. The pH of the preferred ink is from about 7.5 to about 9.0. The preferred pigments used in the inks include those which generate black, cyan, magenta or yellow inks. Such pigments include carbon black, Pigment Blue 15:3 and 15:4, Pigment Red 81 and 122, Pigment Yellow 13, 14 and 74, and the like.

When applying the solution comprising a reactant to a substrate, there is generally no limitation with respect to how the solution comprising a reactant is applied to the substrate as long as a portion of the substrate is covered. Therefore, the solution comprising a reactant may be applied to the substrate with, for example, a brush, sponge, cotton cloth, paper cloth, rubber roller, rubber blade, spray gun or ink jet printhead. Also, the application of the solution may be achieved in the presence of or in the absence of a heat source, such as a heat lamp or hot roller.

While there is no limitation with respect to the substrate used with this invention, other than that the substrate is one which can be printed on, the preferred substrate is paper. Therefore, in a preferred embodiment, the solution comprising a reactant of this invention is used in ink jet printing apparatuses similar to the 2050, 7000 and 5700 Ink Jet Printers commercially available from Lexmark International, Inc. of Lexington, Kentucky. When used in ink jet printing apparatuses, the solution comprising a reactant may be applied to the entire paper sheet or only to portions of the paper sheet where ink is being applied. The paper sheets used in such printing applications may be coated prior to printing or after printing, and coated paper sheets may be sold separately.

In a most preferred embodiment, the entire paper sheet is coated within an ink jet printer prior to printing. Such an ink jet printer comprises a non-heated polyurethane roller which coats the paper with the solution comprising a reactant prior to printing. The ink jet printer further comprises a system for delivering the solution comprising a reactant to the roller, and the roller is typically placed in close proximity with a metering device so that any excess solution may be removed. A more detailed description of such an ink jet printer may be found in commonly assigned United States Patent Application, entitled "COATING APPARATUS FOR USE IN AN INK JET PRINTER", which has previously been incorporated herein by reference.

The amount of solution comprising a reactant applied to the substrate is generally only limited to the extent that a print image may be formed on the solution coated substrate. The amount of solution comprising a reactant applied per square centimeter of substrate is often from about 25 $\mu g/cm^2$ to about 4,000 $\mu g/cm^2$, and preferably, from about 75 $\mu g/cm^2$ to about 2,000 $\mu g/cm^2$, and most preferably, from about 75 $\mu g/cm^2$ to 350 $\mu g/cm^2$, including all ranges subsumed therein.

It is noted herein that when an entire substrate is not coated with the solution comprising a reactant, all of the ink applied to the substrate does not, therefore, have to come in contact with coated sections of the substrate. Often, however, about 50.0 %, and preferably, about 80.0 %, and most preferably, about 100.0 % of the ink applied to a substrate having the solution comprising a reactant coated thereon comes into contact with coated portions. Thus, this invention is also directed to the coated substrates and the coated substrates having print images formed thereon.

When the solution comprising a reactant is applied to a substrate, either before or after printing, the solution works or acts on an ink by, for example, decreasing the stability of the dispersed pigment in the ink. The solution comprising a reactant thereby causes pigment, pigment with dispersant or both to flocculate, i.e. drop out of solution. When dye-based inks are employed, the solution comprising a reactant causes dye to precipitate out of the ink. It is theorized that the unexpected and superior results discovered in this invention (which include at least one of the following characteristics: improved chroma, optical densities, waterfastness, drying time and reduced intercolor bleed) are directly related to the flocculation of the dispersed pigments or the precipitation of dyes from the inks after printing.

The examples below are provided to further illustrate and facilitate an understanding of the present invention. The examples are not intended to restrict the scope of this invention.

EXAMPLE 1

A beaker was charged with 15.0g of aluminum chloride hexahydrate and 84.0g of diethylene glycol. The contents were stirred with a magnetic stir bar and heated to about 60° C to produce a homogeneous solution. A gram of SILWET® L-7607 surfactant, as made commercially available from Osi Specialties, was added while the temperature of

the solution was maintained at about 60° C. The resulting solution is an example of the solution comprising a reactant (polyvalent metal salt) as described in this invention.

EXAMPLES 2-15

The solution comprising a reactant from Example 1 was applied to commercially available paper types. The solution comprising a reactant was applied with a polyurethane roller (across the entire sheet of paper), and the density of the solution applied varied. The coated sheets of paper were placed in a Lexmark International Inc. 5700 Ink Jet Printer and the sheets were printed on with the commercially available pigment-based carbon black ink sold in the 5700 Ink Jet Printer. The data in Table I below depicts the unexpected and superior results obtained when using the solution comprising a reactant (polyvalent metal salt) of this invention.

TABLE I

Example	Paper Type	Optical Density[A]		Drying Time (sec)[B]		Coating Density[C] ($\mu g/cm^2$)
		U	C	U	C	
2	Fore DP	1.46	1.55	55	24	192
3	UC Xerographic	1.44	1.56	73	26	157
4	Lexmark MSP	1.43	1.53	55	14	212
5	Champion Laser	1.28	1.36	50	8	243
6	Tidal DP	1.38	1.49	51	11	215
7	Relay DP	1.10	1.48	23	7	243
8	Laser 100	1.38	1.50	39	7	322
9	Summit Dataprint	1.45	1.53	72	16	283
10	1st Choice	1.45	1.51	47	18	154
11	Neutch 25	1.50	1.49	85	20	142
12	Fox River Trojan Bond	1.38	1.36	60	21	233
13	Lexmark IJ and Laser	1.43	1.55	51	23	263
14	HP Multipurpose	1.37	1.37	65	15	212
15	CompUSA Multipurpose	1.47	1.52	86	21	274

A = Optical densities were measured with a commercially available densitometer. **U** depicts uncoated paper, and **C** depicts paper coated with the reactant solution of Example 1.

B = Drying times were determined by observation and a timing device. **U** and **C** are as previously defined.

C = Density determined by measuring the weight difference of coated and uncoated sheets of paper with respect to a constant volume.

EXAMPLE 16

The solution comprising a reactant in this example was prepared in a manner similar to the one described in Example 1 except that 50g of Superfloc C-567 flocculant (polyquat, as made commercially available) was used as the reactant in lieu of aluminum chloride hexahydrate, and 49.0g of diethylene glycol and 1.0g SILWET® L-7607 were added. The resulting solution comprising a reactant was coated onto sheets of commercially available Crane's Crest paper. The solution comprising a reactant was

coated across the entire sheet of paper (with a polyurethane roller) at a density of about 150 μg/cm^2.

EXAMPLE 17

The solution comprising a reactant in this example was prepared in a manner similar to the one described in Example 16 except that a mixture of 50.0g Superfloc C-567 flocculant and 15.0g aluminum chloride hexahydrate were employed as the reactants in lieu of only Superfloc C-567 flocculant, and 34.0g of diethylene glycol and 1.0g SILWET® L-7607 were added. The resulting solution comprising a reactant (mixture of reactants) was coated onto sheets of commercially available Crane's Crest paper. The solution comprising a reactant was coated across the entire sheet of paper (with a polyurethane roller) at a density of about 150 μg/cm^2.

EXAMPLES 18-19

The coated sheets of paper prepared in Examples 16 and 17 were placed in a Lexmark International, Inc. 5700 Ink Jet Printer. The coated sheets were printed on with the commercially available pigment-based carbon black ink and cyan, magenta and yellow dye-based inks sold in the 5700 Ink Jet Printer. The black ink and color inks were printed in a fashion so that each color ink was at least side by side to the black ink or an ink of different color. The data in Table II below depicts the unexpected and superior results obtained when using the solution comprising a reactant (polyquat or mixture of polyquat and polyvalent metal salt) of this invention.

TABLE II

Example	Paper Type	Optical Density[1] U	Optical Density[1] C	Drying Time (sec)[2] U	Drying Time (sec)[2] C	W/B/F[3] U	W/B/F[3] C
18	Cranes Crest paper	1.25	1.37	18.0	15.0	N	Y
19	Cranes Crest paper	1.25	1.40	18.0	15.0	N	Y

1 = Optical densities were measured with a commercially available densitometer. **U** depicts uncoated paper, and **C** depicts coated paper, Example 18 uses coated sheet of Example 16 and Example 19 uses coated sheet of Example 17.

2 = Drying times were determined by observation and a timing device. **U** and **C** are as previously defined.

3 = **W** is ink waterfastness determined by submerging the paper sheets having the print images in deionized water (ambient temperatures) for about 5 minutes. After removing the sheets, the print images were visually analyzed for ink fading and ink running. **B** is ink bleeding determined by visually analyzing the interaction of the inks of the print images of different colors printed side by side. **F** is the feathering of inks of the print image into the fibers of the paper. **N** is fail, whereby the inks of the print images displayed fading or running, and bleeding and feathering was also visually observed. **Y** is substantially no fading, running, bleeding or feathering of the inks of the print images.

EXAMPLE 20

A reaction vessel was charged with a solution of methacrylic acid 22.8 g (265 mmol), monomethacryloxypropyl-terminated polydimethylsiloxane (PDMS-MA) 7.84 g (8.7 mmol, MW 900), stearyl methacrylate 2.95 g (8.7 mmol), 1-dodecanethiol 2.06 g (9.9 mmol), dimethyl 2,2-azobisisobutyrate 0.64 g (2.84 mmol) and isopropyl alcohol 100 mL. The resulting mixture was degassed with argon (done by repeated partial evacuation followed by argon backfill using a Firestone Valve) then heated to 70^0 C for 16 hours. The mixture was allowed to cool to about room temperature and subsequently added slowly to 1.0 L of hexane while stirring. The resulting solid product (polymeric dispersant) was isolated by vacuum filtration and dried in vacuum overnight at 80^0 C. The yield of the reaction was about 85%. The dried polymeric dispersant (the preferred dispersant in this invention) was characterized by proton NMR and GPC.

A stock solution of the polymeric dispersant was prepared by charging a 400 mL beaker, on a hot plate with a magnetic stirrer, with 40.0 g of deionized water. Added to the beaker with deionized water was 12.0 g of dried polymeric dispersant and 18.0 g of 20% KOH. The resulting mixture was heated to about 50° C for about 2 hours. The pH of the mixture was adjusted to 7.5 by the addition of 20% KOH. Deionized water was

then added to the mixture to bring the weight of the resulting solution to 100.0 g (12% polymeric dispersant).

A beaker was then charged with 133.33 g of the polymeric dispersant solution prepared above, 206.67 g of deionized water and 64.0 g of carbon black. The contents were stirred with a commercial mixer. The resulting mixture was then added to a grinding mill having 0.8 mm yttrium coated zirconium beads. The mixture was ground for about 90 minutes, resulting in a carbon black concentrate.

A second beaker was charged with 10.0 g of polyethylene glycol having a weight average molecular weight of about 400. 10.0 g of 1,3-propanediol were then added while stirring with a magnetic stir bar. After a homogenous mixture resulted, 0.20 g of commercially available biocide solution having 1,2-benzisothiazolin-3-one and deionized water (enough to make a 100g solution) were added with stirring resulting in an ink vehicle.

A third beaker was charged with 18.75 g of carbon black concentrate prepared above, and the entire ink vehicle produced above was slowly added while stirring. The resulting composition was filtered to 1.2 microns using a commercially available pressurized filtration apparatus having a series of disk filters. The resulting filtered solution is a black ink composition (3.0% carbon black) commercially available in the Lexmark International, Inc. 2050 Ink Jet Printer.

EXAMPLE 21

The ink composition of this Example was prepared in a manner similar to the one described in Example 20 except that 25.0 g of carbon black concentrate were used to prepare a black ink composition having 4.0% carbon black.

EXAMPLE 22

A solution comprising a reactant was prepared by adding to a beaker 1.3 % by weight acetic acid (reactant), 2.0 % by weight propanol and the balance being deionized water to make a 100.0g solution. The contents were stirred to produce a homogeneous solution comprising a reactant (mild acid).

EXAMPLE 23

The solution comprising a reactant in this Example was prepared in a manner similar to the one described in Example 22, except that 4.0 % by weight acetic acid was used in lieu of 1.3 % by weight acetic acid, and the balance of water was decreased by 2.7 weight percent in order to produce a 100g solution comprising a reactant.

EXAMPLES 24-32

In Examples 24-32, a commercially available tri-color ink cartridge of a Lexmark International, Inc. 7000 Ink Jet Printer was filled (one reservoir) with either the 1.3 % or the 4.0 % by weight acetic acid solution prepared in either Example 22 or 23. The other reservoirs were filled with black inks as prepared in either Example 20 or 21. The printer was programmed to print a dot of solution comprising a reactant under a dot of black ink. The data in Table III below demonstrates the superior results obtained in this invention, which include increases in optical density (measured as described above). It is noted that drying times were tested in the manner similar to the ones described above for all examples except Examples 25, 26 and 31. The results indicated that the drying times remained substantially the same as the control drying times or were faster than control drying times, while at the same time, the optical density increased.

TABLE III

Example	Paper Type	Optical Density: Control (no undercoat)[i]		1.3% Acetic Acid Solution[ii]	4.0% Acetic Acid Solution[ii]	1.3% Acetic Acid Solution[iii]
24	Hammermill® Tidal DP	1.09	1.19	1.50	1.52	1.45
25	1st Choice	1.55	1.36	1.61	1.54	1.47
26	Champion Ink Jet	1.32	1.18	1.38	1.40	1.47
27	Hammermill® Laserprint	1.44	1.22	1.61	1.56	1.57
28	Hammermill® Xerolasercopy	1.48	1.29	1.61	1.58	1.49
29	Boise Cascade x9000	1.59	1.38	1.57	1.56	1.49
30	Fox River Bond	1.50	1.36	1.37	1.34	1.47
31	Xerox Hi Tech Ink Jet	1.35	1.24	1.41	1.40	1.48
32	Hammermill® Fore DP	1.53	1.33	1.66	1.58	1.51

i = left column 3.0% carbon black, and right column 4.0% carbon black (inks of Example 20 and 21, respectively).

ii = ink composition of Example 20 was used (3.0% carbon black).

iii = ink composition of Example 21 was used (4.0% carbon black).

EXAMPLES 33-35

The pigment-based cyan, magenta and yellow inks of Examples 33-35 were prepared in a manner similar to the one used to prepare the black ink composition in Example 20 except that color pigments were used in lieu of carbon black, and glycerol and 2,2'-thiodiethanol were used as part of the cosolvent system of the magenta ink.

Hammermill® Tidal DP paper was coated with a reaction solution (dropwise with a programmed Lexmark International, Inc. 7000 Ink Jet Printer) similar to the one described in Example 23 except that 4.0 weight percent glycolic acid was used in lieu of acetic acid. The pigment-based color inks of Examples 33-35 were placed (printed) dropwise over the coated portions of the paper. Table IV below lists the ingredients of the color inks and the data in Table V depicts the improvement in color gamut of the print samples having the solution comprising a reactant (glycolic acid) as an undercoat.

TABLE IV

Ink Component	Example 33 CYAN INK	Example 34 MAGENTA INK	Example 35 YELLOW INK
Pigment Blue 15:3	2.0 wt%	—	—
Pigment Yellow 13	—	—	1.5 wt%
Pigment Red 122	—	4.0 wt%	—
Dispersant (Prepared in Example 12)	0.5 wt%	1.0 wt%	0.5 wt%
1,3-Propanediol	10.0 wt%	6.0 wt%	10.0 wt%
Polyethylene Glycol (MW 400)	10.0 wt%	—	—
2,2'-Thiodiethanol	—	8.0 wt%	10.0 wt%
Glycerol	—	6.0 wt%	—
Deionized Water	balance	balance	balance

TABLE V[t]

		L*		a*		b*	
Example	**Ink**	**U**	**C**	**U**	**C**	**U**	**C**
33	Cyan	56.8	53.3	-12.2	-12.7	-36.6	-41.6
34	Magenta	52.4	45.9	43.6	55.7	-5.7	-5.5
35	Yellow	84.3	82.7	-11.8	-13.2	69.8	78.8

t = The data in Table V is provided to describe the improved color gamuts of the color print samples having the solution comprising a reactant of this invention as a paper coat. The characteristics referred to as **L***, **a*** and **b*** (measured with a Minolta Spectrophotometer CM-2002 and using a CIELAB color scale in compliance with ASTM standards) maybe plotted using a Cartesian coordinate system, whereby **a*** is plotted on the x-axis, **b*** is plotted on the y-axis and **L*** is plotted on the z-axis. The resulting points maybe connected and each resulting circumscribed portion may have its area measured. The greater the area, the greater the color gamut. **U** means uncoated paper and **C** means coated paper. Based on the values above, it is apparent that the printed samples printed over coated paper have an unexpected improvement in color gamut.

WHAT IS CLAIMED IS:

1. A method for coating a substrate comprising the steps of applying, in no particular order, to the substrate:

(a) a solution comprising a reactant; and

(b) an ink comprising a colorant,

with the proviso that when said colorant is a dye, said reactant is not a polyvalent metal salt.

2. A method for coating a substrate in accordance with claim 1, wherein said ink comprising a colorant is acidic and said solution comprising a reactant is alkaline.

3. A method for coating a substrate in accordance with claim 1, wherein said ink comprising a colorant is alkaline and said solution comprising a reactant is acidic.

4. A method for coating a substrate in accordance with claim 2, wherein said colorant is a dye or a pigment and said reactant is a base.

5. A method for coating a substrate in accordance with claim 3, wherein said colorant is a dye or a pigment and said reactant is an acid.

6. A method for coating a substrate in accordance with claim 4, wherein said dye is a cyan, magenta or yellow dye, said pigment is carbon black or a cyan, magenta or yellow pigment, and said base is polyethylenimine, a polymer prepared from dimethyldiallylammonium chloride or a mixture thereof.

7. A method for coating a substrate in accordance with claim 5, wherein said dye is a cyan, magenta or yellow dye, said pigment is carbon black or a cyan, magenta or yellow pigment, and said acid is acetic acid, glycolic acid or a mixture thereof.

8. A method for coating a substrate in accordance with claim 2, wherein said colorant is a dye or a pigment and said reactant is an anionic polyelectrolyte selected from the group consisting of acrylamide and a copolymer of an acrylamide and acrylic acid.

9. A method for coating a substrate in accordance with claim 3, wherein said colorant is a dye or a pigment and said reactant is a cationic polyelectrolyte.

10. A method for coating a substrate in accordance with claim 9, wherein said dye is a cyan, magenta or yellow dye, said pigment is carbon black or a cyan, magenta or yellow pigment and said cationic polyelectrolyte is an ammonium salt of a polyalkylenimine, an acidified polyalkylenimine, a polyamine or a quaternary polyamine.

11. A method for coating a substrate in accordance with claim 10, wherein said quaternary polyamine is a reaction product of dimethylamine and epichlorohydrin.

12. A method for coating a substrate in accordance with claim 3, wherein said colorant is a pigment and said reactant is a polyvalent metal salt.

13. A method for coating a substrate in accordance with claim 3, wherein said colorant is a pigment and said reactant is a mixture of a polyvalent metal salt and a cationic polyelectrolyte.

14. A method for coating a substrate in accordance with claim 12, wherein said pigment is carbon black or a cyan, magenta or yellow pigment and said polyvalent metal salt is a group IIA, IIIA or transition metal salt.

15. A method for coating a substrate in accordance with claim 14, wherein said polyvalent metal salt is aluminum chloride.

16. A method for coating a substrate in accordance with claim 13, wherein said pigment is carbon black or a cyan, magenta or yellow pigment, said polyvalent metal salt is a group IIA, IIIA or transition metal salt, and said cationic polyelectrolyte is a reaction product of dimethylamine and epichlorohydrin.

17. A method for coating a substrate in accordance with claim 16, wherein said transition metal salt is aluminum chloride.

18. A method for coating a substrate in accordance with claim 5, wherein said acid is glycolic acid or acetic acid.

19. A method for coating a substrate in accordance with claim 1, wherein said solution comprising a reactant further comprises a surfactant, a penetrant or both.

20. The coated substrate produced from the method in claim 1.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/13214

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B41M 5/00, 3/00; C09D 11/00
US CL :347/96, 100, 105; 427/258, 322, 342, 402; 428/195, 411.1, 500
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 347/96, 100, 101, 105; 427/258, 288, 299, 301, 322, 326, 331, 333, 342, 402; 428/195, 212, 411.1, 413, 500

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,446,174 A (MAEKAWA et al) 01 May 1984, column 4, lines 18-31, c. 5, l. 48-61, Example 5, and claims 1, 3 and 5.	1, 3, 5, 7, 18-20
X	US 5,006,862 A (ADAMIC) 09 April 1991, column 1, lines 43-51, Formulations A3 and A4 in Examples 1 and 2, Formulation A5 (Example 3), and Examples 5 and 6.	1, 2, 4, 20
X	US 5,320,668 A (SHIELDS et al) 14 June 1994, column 2, line 22 to c. 3, l. 29, c. 3, l. 59 to c. 4, l. 6, Examples 2 and 3, and claims 1-4 and 10.	1, 3, 5, 20
X	US 5,439,739 A (FURUKAWA et al) 08 August 1995, column 2, line 40 to c. 6, l. 46, c. 10, l. 25, c. 11, l. 11-15 and Examples 1-6.	1, 2, 4, 6, 8, 19, 20

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

29 JUNE 1999

Date of mailing of the international search report

12 JUL 1999

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231
Facsimile No. (703) 305-3230

Authorized officer
MARIE R. YAMNITZKY
Telephone No. (703) 308-0651

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/13214

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,555,008 A (STOFFEL et al) 10 September 1996, see the whole document, especially column 3, lines 1-37 and c. 5, l. 1 to c. 8, l. 54.	1-6, 8-17, 19, 20
X	US 5,640,187 A (KASHIWAZAKI et al) 17 June 1997, column 2, line 28 to c. 3, l. 3, c. 4, l. 23-36, c. 5, l. 3-67, c. 7, l. 36 to c. 8, l. 37 and c. 10, l. 32 to c. 14, l. 21.	1, 3, 5, 7, 12, 14, 18-20
X	US 5,679,143 A (LOOMAN) 21 October 1997, see the entire document, especially column 3, line 30 to c. 4, l. 20, c. 6, l. 4-32, c. 7, l. 30-67, c. 8, l. 40-54 and c. 9, l. 1-43.	1, 3, 5, 7, 18-20
X	US 5,695,820 A (DAVIS et al) 09 December 1997, see the whole document, especially column 2, line 60 to c. 3, l. 20, c. 3, l. 53 to c. 4, l. 37, c. 5, l. 30 to c. 7, l. 7, c. 7, l. 58-67 and c. 9, l. 1-31.	1, 3, 5, 7, 18-20